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Understanding transition metal dichalcogenide absorption line widths in electron energy loss spectroscopy”

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Two-dimensional transition metal dichalcogenides (TMDs) have attracted great excitement for potential applications in optoelectronic and valleytronic devices. However, localized states in these low dimensional materials are not understood completely. Specifically, the impact of monolayer corrugation and roughness over spatial distances of tens of nanometers has an impact on the optical properties and its role in increasing the absorption linewidths have not yet been fully characterized. In graphene,[1] it has been observed that h-BN encapsulation reduces the monolayer roughness from 114 ± 1 to 12 ± 5 pm,[2] with a typical lateral roughness estimated to be in the tens of nanometers. A direct spatial correlation of these corrugations to their effect on the optical properties of monolayers has not yet been demonstrated.

An ideal technique to map this change is electron energy loss spectroscopy (EELS), which was used to map excitons in TMDs monolayers [3] with a spatial resolution approaching ten nanometers. Typical exciton linewidths in ~micrometer-wide suspended monolayers are above 50 meV, both at 150 and 300 K [3,4]. This is considerably larger than purely optical measurements at similar temperatures for monolayer on substrates [5]. Encapsulated TMDs monolayers show indeed considerably sharper EELS absorption lines, of the order of 20 meV (Figure 1), with spectra comparable to extinction spectra [6]. Is the layer corrugation alone responsible for this line width increase, as these experiments indicate, or are other effects playing a role?

Here we experimentally probed the relation between the line width of the excitations absorption lines and the corrugation in freestanding WS₂ monolayers and WS₂ monolayers supported on a thin h-BN using EELS and electron diffraction in a scanning transmission electron microscope (STEM). Experiments performed on the ChromaTEM microscope, a modified Nion HERMES 200 equipped with an electron monochromator, allowed energy spreads down to below 10 meV, with samples at 150 K. The electron beam parameters were: 60 keV energy and 1mrad convergence half-angle. The EELS spectrometer dispersion was 3.3 meV/pixel EELS. To reveal the effect of corrugation on the monolayers, electron diffraction patterns were acquired with the sample tilted 470 mrad with respect to the electron beam, as demonstrated elsewhere for graphene [1,2].

As seen in Figure 1(a), the peaks identified as A, B, C, and D excitons are considerably sharper on the monolayer region which is supported by h-BN (red), while those of the freestanding are extremely broad and merging (green). These two measurements performed on different regions of the same WS₂ monolayer, were separated by a few hundred nanometers.

Diffraction patterns obtained on these two regions (Figure 1(b-c)), with the sample tilted with respect to the incident electron direction, show a marked difference. For the freestanding monolayer, most of the diffraction spots get larger and fuzzier as a function of their magnitude (for example, those marked by green circles in Figure 1(b)). These spots with the sample orthogonal to the beam propagation direction are sharp (not shown). For the supported

monolayer region, the same diffraction spots (marked by red circles in Figure 1(c)) are unchanged between the tilted and un-tilted configurations. In the diffraction pattern of the supported sample, extra diffraction spots due to the h-BN layer are seen. As the lattice parameters of h-BN and WS₂ are different, the two sets of spots are distinguishable. Finally, the diffraction spots along the sample tilt axis (two of them are marked by green squares in Figure 1 (b)) are not broadened in the freestanding layer, as observed for rough graphene [1,2].

In this contribution, we will discuss the structural differences between freestanding and h-BN supported monolayers and the possible impact on the observed optical exciton line width.

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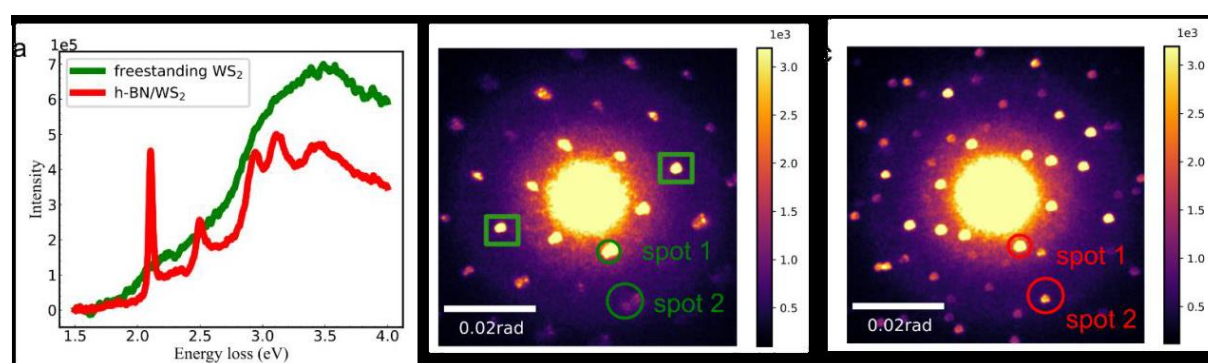


Figure 1. (a) Monolayer WS₂ EELS absorption spectrum of a freestanding (green) and a h-BN support (red) region of the same spectrum. (b) and (c) Diffraction patterns of the two different zones where the spectra in (a) were measured with the sample tilted to 470 mrad with respect to the electron beam propagation direction. The circles in (b-c) mark spots that get broader as a function of the reciprocal space vector magnitude. The spots marked by squares are positions close to the rotation axis of the sample and are not considerably broadened.

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